Rb-Sr AGE DETERMINATION OF DETRITAL MUSCOVITE IN THE PENNSYLVANIAN SHARON SANDSTONE OF OHIO

BY

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ABSTRACT

The Rb-Sr method was used to determine the age of detrital muscovite in the Sharon Sandstone at the base of the Pennsylvanian System in Ohio. The age obtained for the muscovite is 430 million years. This indicates that the muscovite crystallized during the Silurian Period and may have originated from the Appalachian mountain region. Combining this age with the flow patterns of sediment during the Pennsylvanian Period, as described by Potter and Siever (1956), indicates a provenance in the northern region of the Appalachian Mountains including New York, New Hampshire, Vermont, and perhaps even Maine and Nova Scotia.

ACKNOWLEDGEMENTS

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INTRODUCTION

Detrital muscovite from the Sharon Sandstone which is the basal member of the Pennsylvanian System in Ohio was dated by the Rb-Sr method to determine the source area of the sandstone. Possible source areas are the Precambrian Canadian Shield to the north and the Appalachain Mountains to the east and northeast. Several previous studies on the Sharon Sandstone using crossbedding indicate that the sediment was derived from the Appalachain Mountains.

The only previous attempt at dating detrital muscovite has been done by D. G. Brookins and J. P. Voss (1970) on muscovite from the Wamego sandstone of Pennsylvanian age in Kansas. They used both K-Ar and Rb-Sr methods of dating to determine whether dating could be used to distinguish between sheet and channel sandstones and to identify the provenance of the sediment. Their study showed that the provenance of the channel sandstone and the sheet sandstone was similar as indicated by the close agreement of the dates as shown in Table 1. These ages indicate that the muscovite was derived directly or indirectly from Middle or Lower Devonian sources, none of which is known to have supplied clastic material to eastern Kansas.

	K-Ar date (m.y.)	Rb-Sr date (m.y.)
Channel sandstone	377±11	368±20
Sheet sandstone	389±8	401±20

Table 1. K-Ar and Rb-Sr Dates of Muscovites from Channel and Sheet sandstones of the Wamego Formation (Pennsylvanian) of Kansas (Brookins and Voss, 1970).

GEOLOGY OF THE POTTSVILLE FORMATION

The Pottsville Formation consists primarily of cobble and pebble conglomerate, conglomeratic sandstone, and sandstone with minor amounts of shale, siltstone and coal. The basal member of the Pottsville Formation is the Sharon Conglomerate. It consists of interbedded conglomerate, conglomeratic sandstone and sandstone. Rapid transitions from conglomerate to coarse sandstone are typical. The Sharon Conglomerate rests unconformably on Mississippian strata which in general become older as they are traced from south to north. The pre-Pennsylvanian erosion surface shows moderate relief which accounts for the thickness variations of the Sharon Conglomerate.

The conglomerate consists of a matrix which is a weakly cemented orthoquartzitic sandstone. The majority of the pebbles consist of vein quartz (white, milky, and rose). Minor amounts of metaquartzite conglomerate, sandstone, siltstone, shale, jasper, and slate pebbles are also present. Fossils occur in the thicker conglomerate zones and most have been identified as either rugose or tabulate corals, trilobites, and brachiopods. The fossils are Middle Devonian in age. Most of the pebbles are spherical (0.69 - 0.72) and well rounded (0.7) (Meckel, 1967,242).

The sandstones of the Sharon are compositionally mature. They consist predominantly of well-rounded quartz grains with a small quantity of feldspar, rock fragments, mica, and opaque minerals (magnetite, chromite, ilmenite, tourmaline, and zircon). The dominant cement is quartz deposited in optical continuity with the detrital quartz. Locally, iron oxide is an important cement.

Sedimentary and metamorphic rocks are the two major source rocks for the Sharon Conglomerate. The abundance of sedimentary rock fragments

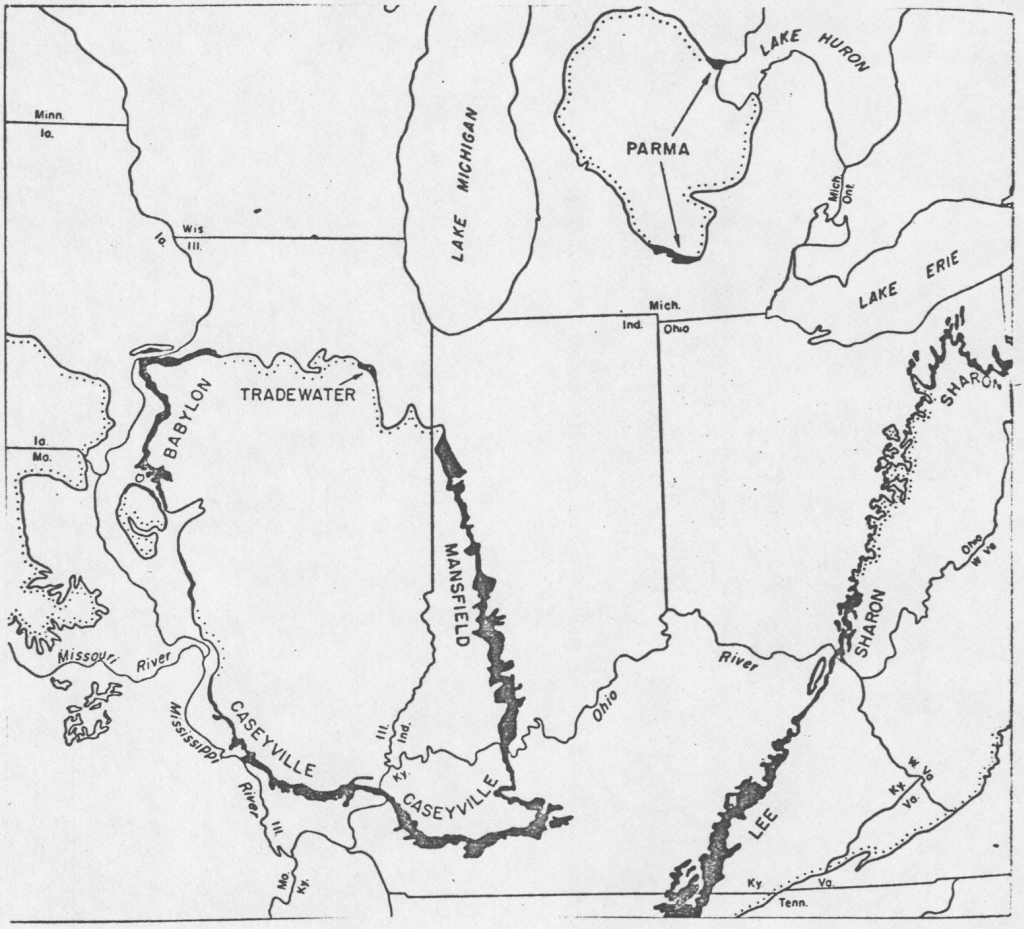

Fig. 1. Extent of the Sharon (Potter and Siever, 1956)

(especially chert) suggests that pre-existing sedimentary rocks contributed significantly to the Sharon. Pebbles containing Middle Devonian fossils are evidence that some of the older Paleozoic strata were being eroded. The chert grains may have originated from the Onondaga Limestone (Middle Devonian) and from the Lockport Group carbonates (Middle Silurian). The sandstone pebbles are similar to Devonian and Silurian sandstones. Additional evidence that the material came from pre-existing sediments is: the high purity of the formation suggesting at least a second generation deposit, the restricted heavy mineral suite, the low feldspar content, both sand grains and pebbles of quartz with secondary crystal faces which are characteristic of quartz derived from a metaquartzite, rare quartz grains with acicular inclusions characteristic of recent igneous rock sources, and the absence of igneous rock fragments, lack of ferromagnesian minerals which indicate that igneous rocks were not common in the source area.

PREVIOUS STUDIES OF THE POTTSVILLE FORMATION

J. S. Newberry in 1873 was the first to speculate on the source of the conglomerate of Carboniferous age. According to Newberry (1873) the pebbles of the conglomerate were derived from quartz veins and had been brought hundreds of miles from an area underlain by metamorphic crystalline rocks. In the process of transportation only the most resistant mineral (quartz) was able to survive the constant grinding. The presence of banded siliceous slate pebbles as well as the internal structure of the quartz pebbles are consistent with this hypothesis according to Newberry. The fossils of the conglomerate are almost entirely plants with the most common being trunks or branches of Lepidodendron, Sigillaria, and Calamites. Newberry (1873) also found traces of marine organisms, shells and crinoids and angular to slightly rounded fragments of chert containing "Sub-carboniferous" fossils which were derived from "Sub-carboniferous" limestone and were broken by the forces that caused deposition of the conglomerate.

Newberry (1873) concluded that the Sharon conglomerate was deposited by ice. Newberry disregarded the idea that this deposit was formed during an invasion of the sea because of its widespread distribution, coarseness, and because of its location many hundreds of miles from any possible source of supply. He also disregarded the transport of the conglomerate by a river system because of the thickness of the deposit and its similarity of composition over all parts of the area it occupies. Newberry also thought that both of these means of transportation would excavate the beds over which they flowed. Newberry's idea of ice transportation and deposition was abandoned when more was learned about

glacial drift. His suggestion that the pebbles were derived from quartz veins is still accepted.

In 1911 G. F. Lamb concluded that the conglomerate is a deposit of stream gravels which were laid down in the creek and river valleys that formed depressions in the Cuyahoga (Mississippian). The overlying sandstones of the Pottsville he interpreted as river and delta deposits. Lamb (1911) found from field work that the Sharon changes structure quickly, disappears suddenly and may also be absent in some areas with younger rocks forming the contact with the Cuyahoga. Lamb also found that the formation occurs in belts which trend approximately north-south which in places were never connected from east to west. In some places the Sharon consists entirely of quartz pebbles ranging from coarse sand to pebbles "half the size of the fist". The formation commonly consists of alternating sand and pebble layers varying constantly both horizontally and vertically. Bottom-set, fore-set, and top-set beds are common. Stream action is the only way Lamb could account for the sudden change from sand to gravel and the variable structure of the sand beds, both of which may be repeated several times in a single rock face.

Wilbur Stout (1916) described the environment of deposition of the Sharon as being marine, his reason being the well-roundedness of the pebbles which indicates abrasion by the rolling action of currents. The highly pronounced cross bedding of the strata also indicates current action. Stout (1916) regarded granitic igneous rocks of Archean age of the Laurentian Highlands as the source of detritus which was transported to the sea. The finer products such as the micas which had been altered or broken into thinner pieces, the feldspars which probably had weathered to kaolinite and the ferromagnesian minerals moved more rapidly

and were widely scattered, perhaps being distributed in deep and quiet waters as the shales and shaly sandstones of the Mississippian rocks. The quartz, being more resistant to weathering, would be coarser and its transportation would be slower. Quartz was localized also on the margins of the basin. Then a general elevation took place and the currents were restricted to narrow shallow passages which now had forces sufficiently strong to transport the coarse quartz and build up a conglomerate.

Fuller (1955) thought that the pattern and alignment of the conglomerate belts suggested distributary channels on a deltaic or alluvial plain. Lenses of orthoquartzite which frequently occur in the conglomerate were believed to be remnants of sandbars or similar features and indicated the rapidly changing conditions of deposition and erosion. According to Fuller (1955) the following characteristics contribute to the explanation of the environment of deposition of the Sharon as being an alluvial or deltaic plain. The fact that the Sharon is a widespread thick deposit with an irregular base and relatively flat top; the radial distribution of the conglomerate belts; the great lateral extent of some of the conglomerate belts; the uniformly high degree of sorting in individual beds; the consistent widespread simple cross-stratification; the widespread initial slopes, and the presence of lag gravels.

Fuller (1955, 173) put all of those facts together in the following explanation as to what was occurring during the deposition of the Sharon:

"The present concept is that of a highland in Canada which was composed of a pre-Pennsylvanian sequence of well-cemented quartzites, sandstones, conglomerates and limestones as dominant types. As this highland was eroded and the material transported to the south, rounded quartz pebbles were formed from the quartzites and the pebbles of the conglomerate, and abundant sand was produced from the sandstone and the

matrix of the conglomerate. Most of the limestone went into solution, but some remnants persisted especially where silicified; among this silicified material were the fossils.

"This material moved southward on an appreciable slope and was deposited in a broad basin near sea level, forming an alluvial or deltaic plain on which the distributary channels shifted position frequently. As these channels shifted, the load built forward in prominent cross beds and layer after layer of cross bedded orthoquartzite was deposited. At times the current eroded the tops of these cross beds, and as the velocity decreased again, nearly horizontal beds were deposited, or sheet wash beyond the active channels spread a similar horizontal layer.

Normally the stream gradient was such that the sand was carried and the pebbles rolled along the bottom to give a mixture of sand with scattered pebbles. Local increase in velocity in a channel sorted out the sand, and the pebbles concentrated in the deeper part of the channel, where they later came to form the conglomerate belts. Increase of velocity on the main plain, away from the channel, also caused erosion, which moved the sand farther south and concentrated the gravel at a lower level in a horizontal layer to form the lag-gravel sheets."

Potter and Siever (1956) theorized that during the Mississippian-Pennsylvanian time interval in the Eastern Interior Basin and surrounding areas erosion took place in two geomorphic cycles. The first and longest cycle resulted in extensive truncation of younger beds at the borders of the basin. This truncation was more extensive to the north than either to the east of west. In the course of this long interval of sub-aerial erosion, an integrated stream pattern was developed. Originally,

this drainage must have been consequent on the regional slope from late Chester source areas and in the direction of the regressing Mississippian epicontinental seas. Epeirogenic uplift, causing rejuvenation of the entire area, initiated a new geomorphic cycle. Rejuvenation resulted in the entrenchment of the existing stream pattern and produced widespread, deeply incised (100-200 ft) channels of unconformity in the north central United States. The pronounced northeast-southwest orientation of these entrenched streams implies that the regional slope for much of the Eastern Interior region during both the erosional cycles was to the southwest.

Evidence available both in outcrop and subsurface indicates that these channels have typical dendritic fluvial patterns. Additional evidence, such as the fact that there is more kaolinite in the sedimentary fill of channels, the absence of marine fossils, the abundance of land fossils and plant remains and the presence of some probably autochthonous coal beds suggest a dominantly fluvial origin for the subsequent fill of these channels. Potter and Siever (1956) decided that the Pennsylvanian drainage system was comparable to the Majomet-Teays drainage system of late Tertiary. This study by Potter and Siever helps to support the next study of the deposition of the Sharon.

The most recent and probably the most complete study on the Sharon of northeast Ohio and the Pottsville of Pennsylvania was done by Lawrence D. Meckel in 1967. He measured cross bedding, pebble size and took into account minor current structures. All of his studies were done in northeastern Ohio.

Meckel thinks that the following features are consistent in supporting the hypothesis of an alluvial environment and that taken together they preclude a marine, eolian, or deltaic origin. 1) Conglomerate

localized in narrow belts which in general parallel the direction of transport; 2) Basal contact is irregular and unconformable; 3) Erosional troughs in underlying Mississippian surface subparallel direction of transport and are loci of maximum gravel accumulation; 4) Downcurrent decrease in maximum pebble size, percentage of conglomerate, and abundance of pebbles other than vein quartz is evident; 5) Distinctive types of minor current structures are present (plant fragments, common cut-and-fill, and upcurrent pebble imbrications indicate that the clastic material was derived from a northern source and dispersed by alluviating streams southward across an irregular erosional surface. The irregular thickness of the deposit is related to the topography of the underlying surface. The fine-grained clastic rocks and autochthonous coal which conformably overlie the coarse channel deposits of sand and gravel probably represent flood plain deposition. Other supporting factors are: 1) Poorly sorted nature of the conglomerate and distinct bimodal size distribution are evident; 2) General upward stratigraphic decrease is evident in percentage of conglomerate, maximum pebble size, and thickness of cross-bedding units; 3) Evidence of indigenous marine fauna is absent.

According to Meckle (1967), the Sharon gravels were deposited on the relatively stable, slowly subsiding northern margin of the depositional basin. The depositional surface in this area dipped southward toward and southwestward along the thalweg of the basin. The gravels here give evidence of deposition by a series of streams radiating from a northern highlands and carrying material obliquely to the thalweg of the basin in Ohio. The fluvial system in Ohio was apparently separate from the one of Pennsylvania and there was little intermixing between them. According to Meckle (1967) the highland that Fuller proposed was actually the area

in which these two river systems had a common edge and thus a thinning of deposits is seen in both areas.

Deposition was initially in the erosional depressions in the underlying surface, then spread over the intervening areas. The deposit successively overlapped younger Mississippian strata to the south. Because of the dominance of marine fauna in the lower Pennsylvanian strata of West Virginia a marine environment lay possibly 100-150 miles to the south at this time.

INTERPRETATION

The age obtained for the muscovite is 430 m.y. which places its origin in the Silurian period if it is assumed that all the muscovite in the Sharon Sandstone is from the same location. Several determinations from the Appalachain area give ages which are very close to the one obtained for the detrital muscovite (Calais, Maine - whole rock Rb-Sr 412±15 m.y. (Spooner and Fairbairn, 1970); Arisaig volcanics, Nova Scotia 430±20 m.y. (Fullagar and Bottino, 1968); pegmatites surrounding the Baltimore gneiss domes 425±20 m.y. (Wetherill, et. al. 1966)). However, none of these areas could have supplied a large amount of muscovite. When weathering and erosion occurred, the surrounding rocks would have been affected by these processes also - thus it seems more likely that this muscovite is not all from the same locality but from a number of different sites and therefore the age is not one of a particular sample but a mixed one.

Stout's (1916) conclusion that the material was brought down from the igneous masses to the north by strong oceanic currents is questionable because of the lack of igneous material in the conglomerate and because the age obtained for the detrital muscovite excludes a single Precambrian source. Also more recent studies of the sedimentary features of the Sharon indicate that it was deposited by streams.

Figure 2 of Potter and Siever (1956) which is based on their extensive analyses of crossbedding of the Sharon and other basal Pennsylvanian formations indicates a probable direction of stream flow from the east and northeast. Meckel's (1967) conclusion about the source area of the Sharon are in accord with this pattern of flow.

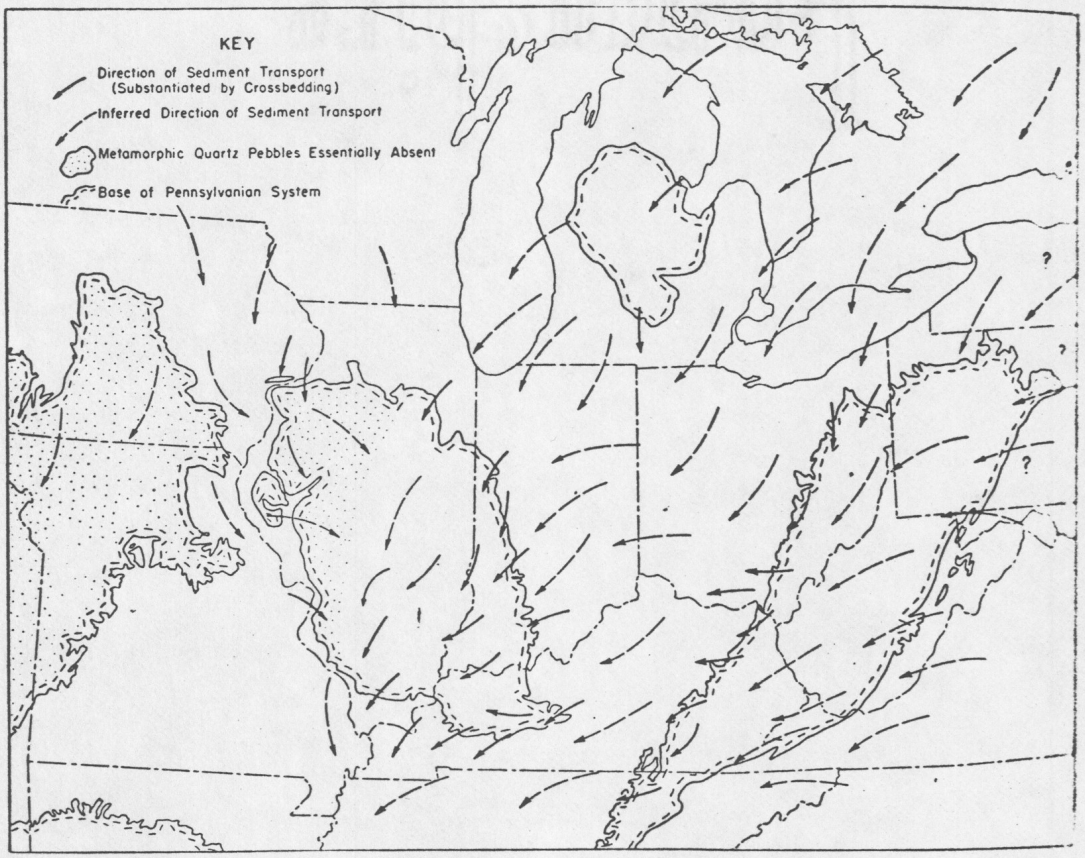

Fig. 2 General flow pattern of sediments at the beginning of the Pennsylvanian Period (Potter and Siever, 1956).

At the present time the Onondaga Limestone and the Lockport Group of carbonates (cherts found in the Sharon conglomerate are from these deposits) lie along an east-west belt 50-70 miles north of the Sharon outcrops in northeastern Ohio. Beyond these carbonate rocks to the northeast lie Cambrian and Ordivician sedimentary rocks, the Adirondack Mountains which are Precambrian, and Paleozoic alkalic, calc-alkalic and metamorphic rocks. The muscovite from these intrusive bodies and metamorphic zones of different ages were probably mixed and deposited in the Sharon Sandstone.

ANALYTICAL PROCEDURE

The sandstone was collected from an outcrop on the south side of a secondary road (Figure 3) $\frac{1}{4}$ mile west of St. John's Church; SW $\frac{1}{4}$ Section 2 T1N, R11W on the Hanover Quadrangle, 7.5 series. This location is approximately two miles due south of Newark, Licking County, Ohio.

The sample from which the muscovite was obtained is a whitish grey to yellowish grey sandstone composed mostly of well to sub-rounded quartz grains with an abundance of muscovite. The sample also contained some dark minerals consisting of ilmenite, chlorite, rutile and zircon. This sample is from the Sharon sandstone which is the basal member of the Pottsville formation in Ohio.

The sandstone was first crushed and screened. The +200 mesh fraction was chosed for separation of muscovite from quartz because micas concentrated in the coarser fraction during crushing and screening. Bromoform was used first in the separation of the muscovite from the quartz. The density of muscovite ranges from 2.76 - 3.1 depending on composition, the density of quartz is 2.65 and that of Bromoform is 2.89. Therefore muscovite may sink while the quartz will float in the Bromoform. The Bromoform was placed in a separatory funnel and some of the crushed sample was then added. The density of the Bromoform was adjusted by the addition of acetone until muscovite began to sink. The material was allowed to settle for approximately $\frac{1}{2}$ - 1 hour, after which the stopcock on the bottom was opened and the settled material and about 3/4 of the Bromoform was let through. The material was collected on filter paper with the Bromoform being collected in an Erlenmeyer flask. The residual material in the separatory funnel was also filtered and the remaining Bromoform was collected. Any sample still left in the separatory funnel was

FIGURE 3


NEWARK
Childrens Home
Sewage Disposal
LICKING RIVER
Oil Wells
Gas Well
Franklin Jr High Sch
Bucks Knob
Radio Tower
Bald Knob
Coffman Knob
US 33
Lloyd Corners
Collection site of sample
NEWARK Swamp
THORNVILLE
GLENFORD
HANOVER
Fleatown

rinsed out with acetone. Both the muscovite-rich and the quartz-rich fractions were taken off their respective filter papers by rinsing with acetone. The fractions were then washed several times to completely remove any remaining Bromoform. Both fractions were then dried by evaporating the acetone on a hot plate.

The sample obtained by the preceeding treatment was about 75-80% pure muscovite. Some quartz was still present due to iron staining which gave it a higher density. The quartz-rich fraction still contained a very small amount of muscovite and it was decided not to try to collect this since some of this muscovite could have been altered.

Next the muscovite-rich fraction was purified by magnetic methods using a Frantz Isodynamic magnetic separator. This was employed since muscovite has a slightly higher magnetic susceptibility than quartz. The magnetic separator was tilted at 10^{o} for all of the different power settings used. At 0.5 amps some of the more magnetic material was separated with only a very small amount of muscovite. When ~~voltage~~ the current was increased to 0.65 amps the muscovite was attracted and further separation from the quartz was obtained. Usually the sample was passed through the separator two or three times at the same amperage to allow for a more complete separation. This gave a sample which was about 90% pure muscovite (purity was checked under an optical microscope).

The final separation of quartz from muscovite was done by shaking on a sheet of paper. Since the quartz grains are essentially round while muscovite grains are flat, the quartz grains roll off and most of the muscovite stays in place when the paper is tilted at a slight angle and shaken. The final muscovite fraction was approximately 97-98% pure.

The muscovite sample was then prepared for analysis on the mass spectrometer. An amount of muscovite (0.6415 grams) was weighed and placed in a teflon dish. To this was added 15 ml of hydrofluoric acid and 3 ml of sulfuric acid. This was left overnight on the hot plate at low heat to dissolve the muscovite. The silicates combined with the hydrofluoric acid and escaped as a gas. Most of the cations left after being released from the silicates remain in solution but some form sulfate compounds.

$$KAl_3Si_3O_{10}(OH)_{2(s)} + 12HF_{(aq)} + H_2SO_{4(aq)}$$

$$K^+_{(aq)} + 3SiF_{4(g)} + 3Al^{+3} + SO_4^{-2} + 8H_2O + 4O_{2(g)}$$

The sulfate residue was dissolved in equal parts of HCl and water and heated. The liquid fraction was reduced to about 15 ml by heating. After filtering, about 5 microcuries of Sr^{89} tracer was added so that the Sr could be followed when this solution was put on the resin column. The Sr fraction was collected from the resin column and evaporated to dryness. This was then dissolved in a very small amount of HNO_3 and placed on the filament of the mass spectrometer for analysis.

Samples of the muscovite were also prepared for isotope dilution analysis of Rb and Sr. For Sr ID the muscovite was weighed (0.3677 grams) and placed in a teflon dish. To this was added a Sr spike (3.8715 grams) which has a Sr^{86} abundance of 97.644% and a Sr^{88} abundance of 1.687%. Then 15 ml of B acid (a combination of HF, H_2SO_4, and HNO_3) was added to the sample. The residue was dissolved in HCl and water. This solution was then filtered and then put on a resin column from which the Sr fraction was again collected.

For the Rb ID the muscovite was also weighed (0.0594 grams). A Rb spike (4.1205 grams) was added in which the Rb^{87} abundance was 99.18% and the Rb^{85} abundance was 0.84%. As in the Sr ID 15 ml of B acid was added to dissolve the muscovite. After collecting the alkali metals from a cation exchange column the solution was placed on a column containing $Zr_2(PO_4)_3^-$. Na^+ and K^+ were removed with 0.5 M HNO_3 and Rb^+ was eluted with 5 M HNO_3. The Rb fraction was then evaporated to dryness and again prepared for mounting on the filament of the mass spectrometer.

DATA

Amount of sample used for Strontium Isotope Ratio Measurement:

0.9891 grams Muscovite and paper
0.3479 grams paper
0.6415 grams Muscovite

Amount of sample used for Rubidium Isotope Dilution:

0.4099 grams Muscovite and paper
0.3495 grams paper
0.0594 grams Muscovite

Amount of Rubidium spike used in Rubidium Isotope Dilution:

7.7351 grams Spike and beaker and cover
3.6146 grams beaker and cover
4.1205 grams Spike

Amount of sample used for Strontium Isotope Dilution:

0.7125 grams Muscovite and paper
0.3448 grams paper
0.3677 grams Muscovite

Amount of Strontium spike used in Strontium Isotope Dilution:

7.4041 grams Spike and beaker and cover
3.5326 grams beaker and cover
3.8715 grams Spike

SrIR Run #2579
#527 Muscovite - Ohio Sandstone
12-13-72

Remarks	IV base	85/100	86/100	87/100	88/IV	Σ85	Σ86	Σ87	Σ88	87/86	86/88	87/86 (corr.)	d	d²
100 mv. base at 50 above zero	33	56	228	189	189								x10⁻⁴	x10⁻⁸
		56	226	186	181									
	33	57	224	185	181									
		58	225	184	179									
	33	55	220	182	180									
(198)	× 33 ×	55	218	177	171	× 37	1041	803	883	.75792	.11789	.7530	2	4
		55	207	173	169			−14						
		54	204	169	164			789						
	33	56	202	168	164									
		56	197	162	157									
	33	55	189	160	155									
(198)	× 33 ×	54	191	159	152	× 30	890	691	763	.76292	.11664	.7532	4	16
		55	193	160	153			−12						
		55	196	160	152			679						
	33	55	195	160	152									
		54	195	159	154									
	33	53	194	159	156									
(198)	× 34 ×	55	194	161	159	× 27	867	659	728	.74740	.11909	.7464	64	4096
		55	421	336	350			−11						
		55	422	334	348			648						
	33	54	412	324	345									
		54	389	299	309									
	33	53	375	299	309									
(199)	× 33 ×	53	378	298	307	× 24	2097	1590	1769	.75393	.11854	.7512	16	256
		54	370	295	306			− 9						
		54	373	296	306			1581						
	33	53	367	296	307									
		53	367	292	301									
	33	55	371	293	301									
(198)	× 33 ×	55	371	295	302	× 24	1919	1467	1626	.75072	.11801	.7542	14	196
		55	364	294	302			− 9						
		55	361	283	292			1456						
	33	55	360	285	293									
		54	355	286	292									
	33	53	358	285	291									
(198)	× 33 ×	53	348	275	282	× 25	1849	1408	1554	.75608	.11898	.7547	19	361
		54	347	275	282			− 10						
		54	345	273	280			1398						
	33	53	342	272	280									
		53	340	270	278									
	33	53	342	272	282									
(198)	× 34 ×	53	349	274	281	× 20	1765	1336	1484	.75240	.11893	.7509	19	361
		53	347	275	282			− 8						
		53	346	273	281			1328						
	33	53	347	273	283									
		53	345	273	281									
	33	53	345	275	281									
(199)	× 35 ×	53	340	270	275	× 18	1770	1239	1487	.75254	.11903	.7513	15	225
		52	342	271	279			− 7						
		52	341	271	277			1332						
	33	52	339	270	279									
		52	337	268	277									
	33	52	339	265	275									
(198)		52	335	263	273	12	1733	1308	1454	.75187	.11918	.7511	17	289
								− 5						
								1303						

Sr Ir #2579
Pg. 2

Remarks	IV/BASE	85/100	86/100	87/100	88/IV	Σ85	Σ86	Σ87	Σ88	86/87	86/88	86/87corr	d	d²
100mv base	33		550	419	442									
			555	433	456									
at 50 Above	33		557	436	458									
zero			558	430	454									
	33		555	430	450									
(198)			554	432	453									
	33	X	552	430	454	X	3029	2286	2515	.75272	.12043	.7559	31	961
			556	432	456									
	33		559	434	458									
			561	435	461									
	33		561	436	463									
(198)			564	436	463									
	33	X	560	436	463	X	3053	2303	2557	.75433	.11939	.7542	14	196
			560	434	462									
	33		560	433	462									
			559	436	463									
	33		565	437	463									
(198)			565	440	464									
	33	X	562	439	466	X	3069	2316	2579	.75464	.11899	.7533	5	25
			565	439	468									
	33		566	441	469									
			570	436	462									
	33		573	444	463									
(198)			573	446	466									
	33	X	569	440	469	X	3109	2345	2596	.75426	.11976	.7553	25	625
			570	437	467									
	33		568	437	463									
			569	445	465									
	33		564	445	464									
(198)			565	444	469									
	33	X	568	442	470	X	3105	2348	2599	.75619	.11946	.7563	35	1225
			569	446	474									
	33		578	449	475									
			577	448	475									
	33		581	448	475									
(191)			579	448	474									
	33	X	573	448	473	X	3153	2381	2645	.75515	.11920	.7545	17	289
			575	445	471									
(94)	33		577	439	473		1575	1182	1318	.75047	.11949	.7507	21	441
											TOTAL	12.0462		9566

AVERAGE 0.7528 ± 0.006

$$\sigma = \sqrt{\frac{\Sigma d^2}{n(n-1)}}$$

Sr-Id Run #2599
Muscovite - Ohio Sandstone #527
1-19-73

Remarks	$S6/_{300}$	$S8/_{300}$	$\Sigma S6$	$\Sigma S8$	$S6/S8$	d	d^2
	373	446					
300 mμ base	395	451					
	400	465					
At 50 above	415	470				$\times 10^{-4}$	$\times 10^{-8}$
	417	491					
zero	× 437	498	× 2137	2521	.8476	10	100
	440	521					
	459	520					
	461	545					
	487	559					
	491	579					
	× 503	579	× 2541	3003	.8461	25	625
	501	590					
	506	587					
	508	589					
	505	595					
	508	551					
	× 479	554	× 2707	3166	.8550	64	4096
	480	561					
	490	565					
	494	579					
	499	580					
	500	579					
	× 493	580	× 2656	3144	.8447	39	1521
	493	575					
	498	576					
	499	581					
	505	581					
	505	582					
	× 499	582	× 2699	3177	.8495	9	81
	500	580					
	499	581					
	499	581					
	503	580					
	499	579					
	× 502	581	× 2702	3182	.8491	5	25
	501	581					
				TOTAL	5.0920		6448
				AVERAGE	0.8486	±.0014	

$$\sigma = \sqrt{\frac{\Sigma d^2}{n(n-1)}}$$

Rb Id Run #2602
#527 Muscovite - Ohio Sandstone
1-25-73

Remarks		$85/300$	$87/300$	$\Sigma 85$	$\Sigma 87$	$87/85$	d	d^2
		101	239					
300 mv base		100	196					
		91	195				$\times 10^{-4}$	$\times 10^{-8}$
at 50 above		90	172					
zero		89	177					
	×	89	176	× 260	855	3.2884	.0380	14400
		91	177					
		91	191					
		97	192					
		97	207					
		100	208					
	×	101	223	× 277	898	3.2418	86	7396
		107	225					
		108	243					
		112	246					
		114	266					
		121	210					
	×	121	292	× 383	1242	3.2428	76	5776
		130	345					
		130	320					
		138	334					
		138	334					
		140	340					
	×	141	348	× 517	1666	3.2224	280	78400
		141	349					
		141	344					
		141	350					
		141	342					
		139	344					
	×	138	333	× 541	1767	3.2661	157	24649
		136	335					
		134	328					
		132	330					
		131	309					
		129	311					
	×	126	295	× 488	1608	3.2950	446	198916
		122	298					
focus		121	282					
		141	410					
200 mv base		140	372					
At 30 above		132	372					
zero	×	131	349	× 567	1863	3.2857	253	124609
		127	351					
		126	343					
		127	347					
		128	344					
		126	341					
	×	134	333	× 578	1879	3.2508	4	16
		124	335					
		125	332					
		124	337					
		124	334					
		126	338					
		125	225	568	1821	3.2235	269	72361

RbID RUN #2602
Pg. 2

Remarks	85/300	87/300	Σ85	Σ87	87/85	d	d²
	124	339					
	124	338					
300 mv base	126	341					
	125	339					
30 above zero	126	341					
	× 125	339	× 570	1857	3.2578	74	5476
	127	341					
	125	341					
	128	347					
	127	342					
	128	346					
	× 129	342	× 584	1879	3.2174	330	108900
	127	345					
	128	344					
	125	344					
	128	344					
	128	345					
	× 127	341	× 586	1883	3.2133	371	137641
	127	343					
	127	340					
	126	340					
	125	339	385	1142	2.9662	Not used	
	×		×				
				total	39.0050		1066112

AVERAGE 3.2504 ± 0.0089

$$\sigma = \sqrt{\frac{\Sigma d^2}{n(n-1)}}$$

CALCULATIONS

STRONTIUM ISOTOPE RATIO MEASUREMENT. From the Sr IR run on the mass spectrometer, peak heights of Rb^{85}, Sr^{86}, Rb^{87} and Sr^{87}, and Sr^{88} were measured. Peak heights were added in groups of six (the height above zero was substracted from this sum so that what was recorded was the sum of the actual lengths of the peak). A correction was made for the Rb^{87} which added to the height of the 87 peak. This was done by use of the known ratio between Rb^{85} and Rb^{87}. Since the natural abundance of Rb^{85} is 0.7215 and that of Rb^{87} is 0.2785, the ratio of Rb^{85} to Rb^{87} is 2.5906. The 85 peak was due only to Rubidium so this could be used as follows to determine how much of the 87 peak was due to Rb^{87}. Rb^{87} = Rb^{85}(sum of peak heights)/2.5906. This number was then subtracted from the sum of the 87 peak heights to give the height of 87 due to Sr^{87}.

Next the ratios of Sr^{87}/Sr^{86} and Sr^{86}/Sr^{88} were calculated. Because the Sr^{86}/Sr^{88} ratio is constant and equal to 0.1194 the ratio of Sr^{87}/Sr^{86} was corrected by using tabulated conversion factors already calculated for the different Sr^{86}/Sr^{88} ratios obtained. The Sr^{87}/Sr^{86} (corrected) ratios were averaged and the standard deviation ($\bar{\sigma} = \sqrt{d^2/n(n-1)}$; where d is the deviation from the average and n is the number of terms) was found. This number can be directly put into the age equation. The ratio of Sr^{87}/Sr^{86} is 0.7528 ± 0.0006.

RUBIDIUM ISOTOPE DILUTION. For Rb ID, peak heights of Rb^{85} and Rb^{87} were measured. As for the Sr IR, these were added in groups of six, again subtracting the height above zero. The ratio Rb^{87}/Rb^{85} was calculated and an average was taken. The standard deviation was also calculated. Results: $Rb^{87}/Rb^{85} = 3.2504 \pm 0.0089$.

The abundance of normal Rubidium is: Rb^{87} 27.85%
Rb^{85} 72.15%

The abundance of the spike Rubidium: Rb^{87} 99.18%
Rb^{85} 00.82%

Since the following are known: 1) Isotope composition of normal Rb, 2) Isotope composition of spike Rb, 3) Amount of sample, and 4) Amount of spike Rb added, the composition of the Rubidium in the mixture can be measured and the concentration of the Rb in the sample can be calculated by relating all the variables in the following way:

$$\left(\frac{Rb^{87}}{Rb^{85}}\right)_M = \frac{Ab_n^{87}N + Ab_s^{87}S}{Ab_n^{85}N + Ab_s^{85}S}$$

($(Rb^{87}/Rb^{85})M$ is measured on the mass spectrometer, Ab_n^{87} is the abundance of normal Rb^{87}, Ab_s^{87} is the abundance of spike Rb^{87}, Ab_n^{85} is the abundance of normal Rb^{85}, Ab_s^{85} is the abundance of spike Rb^{85}, N is the number of normal Rb atoms from the sample and S is the number of spike atoms added.)

The equation is then solved for $(N/S)_{atomic}$:

$$3.2504 = \frac{0.2785N + 0.9918S}{0.7215N + 0.0082S}$$

$$(0.7215N + 0.0082S)(3.2504) = 0.2785N + 0.9918S$$

$$2.3452N - 0.2785N = 0.9918S - 0.0267S$$

$$2.0667N = 0.9651S$$

$$N = \frac{0.9651S}{2.0667}$$

$$(N/S)_{atomic} = 0.4669$$

$$\left(\frac{N}{S}\right)_{weight} = \left(\frac{N}{S}\right)_{atomic}\left(\frac{\text{Atomic weight } Rb_n \text{ x Avogadro's number}}{\text{Avodadro's number x Atomic weight } Rb_s}\right)$$

The atomic weight of Rb_n (normal Rubidium) is 85.4679 amu. The atomic weight of the spike Rubidium (Rb_s) is 86.8926 amu.

$$\left(\frac{N}{S}\right)_{weight} = 0.4669\left(\frac{85.4679}{86.8926}\right)$$

$$(N/S)_{weight} = 0.4592$$

$$N = 0.4592S$$

S is the weight of the spike in micrograms. The concentration of the spike is 7.9 μg/g. The amount of spike added was 4.1205 g. S = 7.9 μg/g x 4.1205 g. S = 32.552 μg

$$N = (0.4592)(32.552)\ \mu g$$

$$N = 14.948\ \mu g$$

The concentration of Rubidium in the sample is equal to the weight of N in μg divided by the weight of the sample in grams.

$$\text{Concentration} = \frac{14.948\ \mu g}{0.0594\ g}$$

Concentration of Rubidium in the sample is 251.65 μg/g.

STRONTIUM ISOTOPE DILUTION. The peak heights of Sr^{86} and Sr^{88} are measured for Sr ID. As for Sr IR and Rb ID these peak heights were added in groups of six with the height above zero subtracted. The ratio of Sr^{86}/Sr^{88} was calculated and the average was also calculated, along with the standard deviation. The results were: $Sr^{86}/Sr^{88} = 0.8486 \pm 0.0014$.

Normal Strontium has four isotopes: Sr^{84}, Sr^{86}, Sr^{87}, and Sr^{88}. The abundance of Sr^{86} is 9.861% and that of Sr^{88} 82.593%. These two isotopes make up 92% of the total amount of Strontium. The Strontium spike that was used contained Sr^{86} with abundance 97.644% and Sr^{88} with an abundance of 1.687%. The following equation is used to find the concentration of Strontium in the sample (calculations are the same as the ones done for Rubidium ID).

$$\left(\frac{Sr^{86}}{Sr^{88}}\right)_M = \frac{Ab_n^{86}N + Ab_s^{86}S}{Ab_n^{88}N + Ab_s^{88}S}$$

$((Sr^{86}/Sr^{88})M$ is measured on the mass spectrometer, Ab_n^{86} is the

abundance of the normal Sr^{86}, Ab_s^{86} is the abundance of spike Sr^{86}, Ab_n^{88} is the abundance of the normal Sr^{88}, Ab_s^{88} is the abundance of spike Sr^{88}, N is the number of atoms of normal Strontium from the sample, and S is the number of atoms of spike Strontium added).

Solving the equation for $(N/S)_{atomic}$:

$$0.8486 = \frac{0.09861N + 0.97644S}{0.82593N + 0.01687S}$$

$$\left(\frac{N}{S}\right)_{atomic} = 1.5975$$

$$\left(\frac{N}{S}\right)_{weight} = \left(\frac{N}{S}\right)_{atomic}\left(\frac{\text{Atomic weight } Sr_n \text{ x Avogadro's number}}{\text{Avogadro's number x Atomic weight } Sr_s}\right)$$

The atomic weight of normal Strontium (Sr_n) is equal to 87.6150 amu. The atomic weight of the spike Strontium (Sr_s) is equal to 85.3683 amu.

$$\left(\frac{N}{S}\right)_{weight} = (1.5975)\left(\frac{87.6159}{85.3983}\right)$$

$$N = S(1.6396)$$

S is the weight of the spike Sr in micrograms. The concentration of the spike solution is 5.16 µg/g. The amount of spike used was 3.8715 g; therefore S = 5.16 µg/g x 3.8715 g. S = 19.98 µg Substituting:

$$N = 19.98\ \mu g \times 1.6396$$

$$N = 32.7533\ \mu g$$

The concentration of normal Strontium is equal to the weight in µg (N) divided by the weight of the sample.

$$\text{Concentration} = \frac{32.7533}{0.3677}\ \mu g/g$$

Concentration of the Strontium in the sample is 89.08 µg/g.

AGE DETERMINATION. The equation for the age determination is:

$$\frac{Sr^{87}}{Sr^{86}_m} = \frac{Sr^{87}}{Sr^{86}_o} + \frac{Rb^{87}}{Sr^{86}}(e^{\lambda t} - 1)$$

$$\left(\frac{Rb^{87}}{Sr^{86}}\right) = \frac{\text{Conc. Rb x Avagadro's number x At. abundance } Rb^{87} \text{ x wt. } Sr^{86}}{\text{Conc. Sr x Avagadro's number x At. abundance } Sr^{86} \text{ x wt. } Rb^{87}}$$

$$\left(\frac{Rb^{87}}{Sr^{86}}\right) = \frac{251.65\ \mu g/g \times 0.2785 \times 87.6758\ \mu g/mole}{89.08\ \mu g/g \times 0.0986 \times 85.4674\ \mu g/mole}$$

$$\frac{Rb^{87}}{Sr^{86}} = 8.176$$

$$\frac{Sr^{86}}{Rb^{87}} = 0.1223$$

The initial value of Sr^{87}/Sr^{86} is assumed to be 0.7040; the value for λ is 1.39×10^{-11}/year.

Substituting:

$$0.7528 = 0.704 + 8.176(e^{1.39 \times 10^{-11}/yr \times t} - 1)$$

$$t = \frac{1}{1.39 \times 10^{-11}} \ln\left[1 + 0.1223(0.7528 - 0.7040)\right] \text{ year}$$

$$t = 4.3 \times 10^{8} \text{ years}$$

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